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[Claim(s)]

[Claim 1] Metal or half-metal (nonmetallic) which is easy to make carbide to conductive fine ceramics, [the metal which is easy to unite processed metal or said fine ceramics] as a binder What was mixed by powdered voice, respectively, performed compression molding, and was made into desired form is used as an electric discharge electrode. [processed metal] by performing electrical discharge machining as one electrode in working fluid using the working fluid which carries out decomposition generation of the carbon by generating of electric discharge as working fluid The surface treatment method of the metal material by the electric discharge among liquid which carries out reaction generation by using as carbide some of metal which is easy to make the aforementioned carbide, or half-metal, and is characterized by forming the surface coat which becomes a processed surface of metal from conductive fine ceramics, carbide, and the metal which did not become carbide in part and joint metal.

[Claim 2] The way according to claim 1 conductive fine ceramics consist of one sort of WC, TiC, TaC, ZrC, VC, TiB2, TiN, and Ti2N, or two sorts or more.

[Claim 3] Metal or half-metal which is easy to make carbide to non-conductive fine ceramics, As a binding material, processed metal and the metal which is easy to unite are mixed by powdered voice, respectively. By performing electrical discharge machining by using one side of processed metal as an electrode into working fluid using the working fluid which carries out decomposition generation of the carbon by generating of electric discharge as working fluid, using what performed compression molding and was made into desired form as an electric discharge electrode The surface treatment method of the metal material by the electric discharge among liquid which carries out reaction generation by using as carbide some of metal which is easy to make the aforementioned carbide, or half-metal, and is characterized by forming the surface coat which becomes a processed surface of metal from non-conductive fine ceramics, carbide, and the metal which did not become carbide in part and binding-material metal.

[Claim 4] The way according to claim 3 non-conductive fine ceramics consist of one sort of Al2O3, Si3N4, and ZrO2, or two sorts or more.

[Claim 5] The way according to claim 1 or 3 the metal which is easy to make carbide consists of one sort of Ti, Nb, W, V, Zr, Ta, Cr, Mo, and Mn, or two sorts or more, and half-metal (nonmetallic) consists of B.

[Claim 6] It is a method according to claim 1 or 3 of the metal which is easy to unite processed metal or said fine ceramics consisting of Fe, Co, or nickel, when processed metal is steel, and consisting of aluminum, Zn,

or Cu in the case of aluminum material, and consisting of Cu, aluminum, or Sn in the case of zinc material.
[Claim 7] The method according to claim 1 or 3 of adding Nb 1 to 10% as a metal which is easy to make carbide.
[Claim 8] The surface treatment method of the metal material by the electric discharge which performs electrical discharge machining for the electrode which is hard to exhaust in liquid or mind as one electrode, and is characterized for a surface coat by re-melting and making it solidify after forming a surface coat by a method according to claim 1 or 3.

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the processing method of the metal material by electric discharge among liquid, and in more detail On the surface which fabricated predetermined form in the metal material which consists of steel, aluminum or its alloy, zinc or its alloy, copper, or its alloy It is related with the surface treatment method which covers the enveloping layer containing fine ceramics, such as WC and TiC, so that it may have firm adhesive strength, and is suitable for raising abrasion resistance, such as metal mold and a gas turbine, thermal resistance, etc.
[0002]
[Description of the Prior Art] Conventionally, a physical variance or chemical surface treatment, such as thermal spraying or PVD, and CVD, are performed for covering to base materials, such as fine ceramics, and plating was also performed to it.
[0003] However, although thermal-spraying technology had a high membrane formation speed and the thick film was obtained easily, adhesion was weak, and a film is porosity and the degree of hardness etc. had the fault which does not arrive to the original degree of hardness of a covering material. Although adhesion is good in many cases, since PVDCVD is raised to a high temperature of about 1000 degrees C and is covered, its dimensional change of a material is remarkable. There was a fault which can generate only a thin film of 10 more micrometers or less. Moreover, plating had the fault that adhesion power was weak, in the top in which the thick film is impossible.
[0004] Furthermore, with such technology, thermal spraying requires vacuum devices for reduced pressure plasma, work is done in a vacuum chamber, plating is also the work in an electrolytic cell, PVDCVD also has bad workability, and automation is also difficult.
[0005] Then, this invention person etc. proposed the electric discharge covering method in Tokuganhei3-329499 previously as technology which cancels faults, such as these thermal spraying, PVD, and CVD. This method is a method which diffuses covering material, is mixed with a base material, and forms a precise enveloping layer in the base material surface by carrying out re-melting of the sediment for every infinitesimal area by pulse discharge processing in liquid, gas, or a vacuum, after covering metal or a nonmetallic substance on the base material surface which consists of metal material.
[0006] This electric discharge covering method has the remarkably high adhesion of an enveloping layer compared with the above-mentioned conventional technology, the thick film which is about 10-100 micrometers is also possible, and accuracy of dimension and accuracy of form are equivalent to the processing precision of electrical discharge machining, are remarkably good, and easy to automate. [of

workability] The above-mentioned conventional technology and comparison of the electric discharge covering method are shown in drawing 1 and Table 1.

[0007]

[Table 1]

表1　各種の被覆法の比較

	PVD法	CVD法	メッキ法	溶射法	放電被覆法
膜厚	薄膜 (5μm程度)	薄膜 (5μm程度)	薄膜 (5μm程度)	厚膜 (50μm以上)	薄、厚膜 (10～100μm)
成膜速度 (μm/min)	低～中 0.01～0.1	中程度 0.25	低～高 0.02～4.0	非常に高い ～1.0mm/min	高い ～5.0
膜の密度	高い	高い	高い	余り高くない	高い
膜の密着性	非常に良い	良い	比較的良い	良くない	非常に良い
膜と母材との混合	有り	有り	有り	無し	有り
寸法精度	悪い	悪い	良い	悪い	良い (放電加工の加工精度)
作業性	悪い	悪い	良くない	悪い	著しく良い
自動化の難易	悪い	悪い	良くない	悪い	著しく良い

[0008]

[Problem to be solved by the invention] However, [the method] although the aforementioned electric discharge covering method is the surface treatment technology which was very excellent compared with the conventional thermal-spraying method, PVD, CVD, and plating On the other hand, when the electric discharge depositing method (electrode use which is easy to exhaust) in the inside of liquid is performed as a prior covering method (1 next processing), the carbon content which the mineral oil of working fluid etc. decomposes and produces by electric discharge may remain as a carbon unit in an enveloping layer as it is. Of course, although it mostly dissolved in the enveloping layer component by secondary treatment (re-melting by pulse discharge processing), it became clear that it may exist in an enveloping layer as a still in addition detailed lump.

[0009] This invention cancels the fault of the above-mentioned electric discharge covering method, decreases that the decomposition carbon produced by electric discharge remains as a lump in an enveloping layer, and aims at offering the surface treatment method of the metal material which forms a more nearly high-definition enveloping layer in a metal material list side.

[0010]

[Means for solving problem] As said The means for solving a technical problem, [this invention] Metal or half-metal (nonmetallic) which is easy to make carbide to conductive fine ceramics, [the metal which is easy to unite processed metal or said fine ceramics] as a binder What was mixed by powdered voice, respectively, performed compression molding, and was made into desired form is used as an electric discharge electrode. [processed metal] by performing electrical discharge machining as one electrode in working fluid using the working fluid which carries out decomposition generation of the carbon by generating of electric discharge as working fluid Carry out reaction generation by using as carbide some of metal which is easy to make the aforementioned carbide, or half-metal, and to a processed surface of metal Conductive fine ceramics and carbide, The surface treatment method of the metal material by the electric discharge

among liquid characterized by forming the surface coat which consists of metal which did not become carbide in part, and joint metal is made into the summary.
[0011] Moreover, metal or half-metal with which other this inventions tend to make carbide to non-conductive fine ceramics, As a binding material, processed metal and the metal which is easy to unite are mixed by powdered voice, respectively. By performing electrical discharge machining by using one side of processed metal as an electrode into working fluid using the working fluid which carries out decomposition generation of the carbon by generating of electric discharge as working fluid, using what performed compression molding and was made into desired form as an electric discharge electrode Carry out reaction generation by using as carbide some of metal which is easy to make the aforementioned carbide, or half-metal, and to a processed surface of metal Non-conductive fine ceramics and carbide, The surface treatment method of the metal material by the electric discharge among liquid characterized by forming the surface coat which consists of metal which did not become carbide in part, and binding-material metal is made into the summary.
[0012] Furthermore, after other this inventions form a surface coat by the above-mentioned method, they perform electrical discharge machining for the electrode which is hard to exhaust in liquid or mind as one electrode, and are characterized for the surface coat by re-melting and making it solidify.
[0013]
[Function] This invention is explained still in detail below.
[0014] This invention other metal, fine ceramics, etc. using the included electric discharge electrode on the surface of the charge of non-iron material of those alloys, such as charges of iron material, such as steel, aluminum, zinc, and copper, [with electric discharge among liquid] It is the method of performing surface coating of metal material, by performing melting of a cladding material, and diffusion and forming a firm and precise surface treatment layer. That is, you re-fuse the enveloping layer formed in the surface using spark discharge energy, and it is made to be spread in a base material, and it is precise and the high enveloping layer of adhesion is formed.
[0015] A laser beam and an electron beam are irradiated at the enveloping layer formed by the thermal-spraying method etc., and to raise the compactness and adhesion of an enveloping layer is tried melting and by making it spread in the surface until now. However, the problem in which the rifle mark on a bullet of a beam remains, and the problem that application on the object of arbitrary form is difficult are shown in the surface, and it did not result in utilization.
[0016] Paying attention to the pulse discharge used as conventional processing technology, this invention person etc. urges re-melting and diffusion of a cladding material with the energy of electric discharge, and finds out that it is possible to perform precise and firm surface coating.
[0017] The surface treatment process by this invention is based on the following mechanisms.
** Form enveloping layers, such as metal, carbide, and a nitride, on the surface of a base material with the electric discharge coating method by a green compact electrode.
** Subsequently the inside of liquid or aerial discharge performs re-melting and diffusion of an enveloping layer.
** If needed, after that, perform the electrical discharge machining in liquid as one electrode, and make an expected size and finish surface roughness to the electrode which is hard to exhaust.
[0018] In order to form an enveloping layer in the surface by the first process **, electric discharge is made to cause between base materials using the thing and sintered compact which pressed the powder of the

material of the enveloping layer to form as an electrode first. Then, the material by the side of an electrode does melting and scattering of with the energy of electric discharge, and it deposits on the base material surface. Next, a pulse discharge is made to cause as ** the base material with which the enveloping layer was formed by ** in liquid, such as kerosene, or mind, using non-consumable electrodes, such as copper, as one electrode. With the energy of a pulse discharge, since the minute field near the enveloping layer surface becomes high temperature and high pressure momentarily, an enveloping layer re-fuses and is spread in a base material. As a result, it is precise and the high surface coat layer of adhesion is formed. It is because the direction in mind is harder to be cooled than the inside of liquid, so the meaning of aerial discharge may be effective if it is the purpose of re-melting. If needed, after that, by process **, electric discharge among liquid is again performed with the material which cannot exhaust [copper] an electrode easily, and an expected size, thickness, and finish granularity are made. Since impulse force is stronger than aerial discharge, this will produce an effect like forging and will form a firm enveloping layer.

[0019] However, [the conventional electric discharge covering method] since binding material is added to carbide and it is a request, as Co was only mixed to WC They are an adequate amount, in addition the thing which is mixed and is made into a green compact about the metal which is easy to make carbide on the powder-compacting fabrication object which uses the decomposition carbon of processing oil as an electric discharge electrode by this invention in view of having been inadequate for considering it as carbide and carrying out absorption combination as other components. Since an addition metal combines with the carbon produced by disassembly of processing oil at the time of electric discharge and it becomes carbide, it stops almost generating the intervention of the carbon as a lump thereby. Furthermore, if ** process is added, carbon can consider it as the enveloping layer which does not exist further.

[0020] The Reason for limitation of the manufacture conditions in this invention is explained below.

[0021] Electric discharge electrode : Metal or half-metal (nonmetallic) which is easy to make carbide to conductive or non-conductive fine ceramics as an electric discharge electrode, As a binder, the metal which is easy to unite processed metal or said fine ceramics is mixed by powdered voice, respectively, and what performed compression molding and was made into desired form is used.

[0022] As conductive fine ceramics, one sort of WC, TiC, TaC, ZrC, VC, TiB2, and TiN or two sorts or more are mentioned, for example. Moreover, as non-conductive fine ceramics, one sort of Al2O3, Si3N4, and ZrO2 or two sorts or more are mentioned, for example.

[0023] As a metal which is easy to make carbide, one sort of Ti, Nb, W, V, Zr, Ta, Cr, Mo, and Mn or two sorts or more are mentioned, for example. Moreover, B is mentioned as a half-metal (nonmetallic) which is easy to make carbide. In order that especially Nb may raise the toughness of a covering surface coat, it is an effective component, and adding 1 to 10% is recommended. Other components are added in general considering this amount of addition as a standard.

[0024] A suitable thing is selected according to the quality of the material of processed metal that what is necessary is just the metal which is easy to unite processed metal or said fine ceramics as a binder. For example, when processed metal is steel, in the case of Fe, Co, or nickel to aluminum material, in the case of aluminum, Zn, or Cu to zinc material, it selects from Cu, aluminum, or Sn.

[0025] Electrical-discharge-machining liquid: Use the liquid which disassembles carbon by generating of electric discharge as working fluid used for electrical discharge machining. For example, they are oil, oil and fats, etc. Since oil is a hydrocarbon (CnHm), if it pyrolyzes, it will produce Cn_x of C, H, and a middle band, and Hm_y. The carbon and the chemical reaction which the metal which is easy to carbonize decomposed

in the ultrashort time amount [bombardment / through a processing gap / in the state of high temperature / with electric discharge / time amount / a processed surface of metal] are caused. Since it is remarkably activated for high temperature, several 10% of this metal serves as carbide.
[0026] the carbide of the metal which is easy to make carbide, or half-metal half-metal M3:binding-material metal M2C:carbide [0027] M1+M2+M3->M1+M2C+M2+M3 -- the metal which is easy to make M1:fine-ceramics M2:carbide here -- or Other electrical-discharge-machining conditions: Other conditions of electric discharge among liquid are the same as that of the electric discharge covering method proposed previously, are good, and are desirable. [of pulse discharge processing] For example, when electric discharge is generated in about tens of thousands of times from hundreds of times in 1 second, a processed surface is the surface which small microscopic electric discharge marks accumulated, and electric discharge marks current density is a minute area, but it is as high as tens of thousands A/cm2, and high temperature high pressure is produced in a short time for several 10 microseconds - about 1000 microseconds. Although the skin temperature of a discharging point turns into boiling point temperature of the material, the pressure of the point is set to several 1000 kgf/cm2 and the dissolved part has some dispersing, the portion which remained is re-fused and is diffused in a base material. Since a charging time value is a short time, a discharging point is cooled immediately and the mean temperature of a base material does not rise.
[0028] The desirable conditions of pulse discharge processing are supply voltage:60-100V, pulse discharge current value (Ip):1 - 100A, pulse width (taup):5-2000microsecond, and quiescent-time (taur):5-2000microsecond. Generally, when the pulse discharge current value Ip is small (for example, when taup=16microsecond and Ip are large in Ip=3A), when Ip is small, by Ip=50A, taup also takes long taup like taup=2000taus, when short **** and Ip are large.
[0029] In addition, the thing of the quality of the material which cannot exhaust [copper] easily the electrode which is hard to exhaust in process ** as an electrode when performing the electrical discharge machining in liquid as one electrode is only used, and other electrical discharge machining conditions are almost the same as the discharging condition in liquid of the aforementioned **, and good. However, since it is the purpose that the process of ** processes enveloping layer thickness and finish surface roughness into an expected value fundamentally, processing will certainly be processed in liquid. Moreover, electric conditions and the thing which becomes settled by expected finish surface roughness mind about a certain thing.
[0030] An example of the equipment used for operation of this invention is shown in drawing 2 . The processed metal (base material) which had the surface made into predetermined form in the work tank which accommodated the working fluid which carries out decomposition generation of the carbon by generating of electric discharge is placed, and, on the other hand, the electric discharge electrode which pressed powder is held to the base material upper part in an about several 10-100-micrometer minute gap. A base material and an electric discharge electrode are movable vertically and horizontally by a move mechanism respectively. Electrical discharge machining is performed by making an electric discharge electrode into a minus pole. In order to exchange for the electrode which cannot exhaust this electric discharge electrode easily, the electrode replacement mechanism is established.
[0031]
[Working example] Next, the work example of this invention is shown.
[0032]
[The example 1 of an examination] Fe powder (average particle diameter of 9.8 micrometers) which consists of WC powder (average particle diameter of 3 micrometers) and malleable iron was mixed to the bulk

density of 1:1, what was compressed by compression pressure 4 ton/cm2 was used as the fine-particles electrode, and, on the other hand, electric discharge processing (primary processing) was performed in electrical discharge machining oil (kerosene) by making processed metal into carbon steel. The discharging condition at this time was set to discharge current Ip=20A and discharge current pulse width taup=16microsecond, and made the fine-particles electrode the minus pole.

[0033] The fine-particles electrode was changed to the non-consumable electrode (copper) after this primary processing, and electric discharge processing (secondary treatment) was performed in the same electrical discharge machining liquid. The discharging condition at this time was set to discharge current Ip=10A and taup=1024microsecond.

[0034] The cross section of the field analysis result by EPMA of the enveloping layer which performed primary processing and secondary elaboration to drawing 3 is shown. (1) is a secondary electron image, (2), C and (4) are the field analysis results of Fe W and (3), a small hole is seen in the secondary electron image of (1), and, as for this, the field analysis result of C of (3) shows that he is the lump of carbon. As shown in the above-mentioned primary processing conditions, in spite of mixing Fe powder of malleable iron, the lump of carbon exists. When content carbon increases in number, steel has the property which cannot make carbide easily so that a graphite may be deposited and it may become graphite cast iron. Of course, although a part serves as a cementite, in addition, it has still left carbon as a lump.

[0035] The Reason a carbon lump remains is considered as follows. Co cannot make carbide easily like Fe powder of malleable iron, either. Therefore, also in the green compact of the mixture of WC+Co, it is the same. When the tendency which is generally easy to make carbide is shown, it is as follows, and it is easy to make carbide as a left-hand side element. nickel, Co, and Si especially on the right of Fe do not form peculiar carbide, but promote graphitization rather.

Nb>Ti>V>W>Mo>Cr>Mn>Fe>nickel>Co>Si [0036] It is as follows when a periodic table shows the element which is easy to make carbide.

IVB group: It is the material which the thing except Hf, Tc, and Re tends to obtain on Ti, Zr, and HfVB group:V, Nb, Ta, VIB group:Cr, Mo, WVIIB group:Mn, Tc, and Re practical use target.

[0037]

[The example 2 of an examination] Then, based on the result of the example 1 of an examination, the element which is easy to make carbide was added as a constituent element of a fine-particles electrode, and electric discharge among liquid was performed using this fine-particles electrode. That is, Ti was chosen as an element which is easy to make carbide, in order to show clearly whether Ti carbonized or not, aluminum without the possibility of carbonizing was also used together, the green compact electrode which consists of Ti and aluminum was made, and processed metal (base material) was also made into aluminum material (aluminum die-casting material ADC12). At that time, the combination object of the carbon by mineral oil decomposition was kept from existing in addition to the carbide of Ti, and the experiment considered so that analysis might become clear was conducted. Moreover, it enabled it to analyze the existence rate in the surface of TiC quantitatively. The mixing ratio of Ti and aluminum at this time, the electrical discharge machining conditions, etc. are as follows.

[0038] The charge of an electrode material: Purity of 99.5% and aluminum was made into 99.7%, and compacting pressure set Ti:aluminum=36:64 (weight %), however purity of Ti also to Ti and aluminum with 441MPa with the powder grain size of 44 micrometers or less.

(%) Rp=D={taup/(taup+taur)} x100% [0039] processing oil: -- kerosene electrical discharge machining

condition for electrical discharge machining: -- discharge current Ip=20A and effective discharge current pulse width taup= 512-microsecond pulse width Rp(duty factor) = -- [here] 33% if the quiescent time is set to taur Drawing 4 is the X diffraction figure of the obtained base material surface coat layer, and it turns out that what was generated by the surface of aluminum material of a base material is TiC and TiAl3.

[0040] Furthermore, the result of having changed discharge current pulse width taup among electrical discharge machining conditions, and having investigated the thickness of an enveloping layer and the volume ratio of TiC is shown in drawing 5 . Moreover, the result of having changed the floor to floor time tw and having investigated the thickness of an enveloping layer and the volume ratio of TiC is shown in drawing 6 . The volume ratio of TiC in an enveloping layer is 50% or more, and these test results show having reached to about 70%.

[0041] Thus, the carbon under enveloping layer organization serves as carbide enough, and that a great portion of Ti is TiC shows that it has the powerful operation which does not produce the carbon of isolation. The degree of hardness of the carbide produced in this way is also high enough, and micro Vickers hardness shows 500 to 1000 or more. In the byte material already put in practical use, if the property which was excellent in high temperature abrasion resistance when TiC other than WC and Co was added is shown, it has similarly the property which was excellent also in this enveloping layer.

[0042]

[The example 3 of an examination] The green compact electrode which mixed WC and each powder of Co and Ti at a rate of WC:Co:Ti=60:20:20 (weight %), respectively was made, this was made into the electric discharge electrode, and electrical discharge machining (primary processing) was performed in processing oil (kerosene). Carbon steel (S55C) was used for processed metal. The electrical discharge machining conditions at this time were set to discharge current Ip=20A and discharge current pulse width taup=16microsecond, and made the fine-particles electrode the minus pole.

[0043] The fine-particles electrode was changed to the non-consumable electrode (copper) after this primary processing, and electric discharge processing (secondary treatment) was performed in the same electrical discharge machining liquid. The discharging condition at this time was set to discharge current Ip=10A and taup=1024microsecond.

[0044] TiC was generated like the example 2 of an examination by the X diffraction result of the base material surface coat layer obtained by the primary secondary elaboration. Moreover, in the SEM image (electron microscopic picture) of the cross section, a cavity was not seen but it was checked that carbon residue does not exist. The result whose abrasion resistance as a cutting tool of about 10 times is high was obtained rather than the enveloping layer formed at a rate of WC:Co=80:20 without this enveloping layer adding Ti. The cutting test condition at this time was made into 0.5mm of cuts, delivery 0.1 mm/min, and cutting speed 100 m/min, using the round bar of carbon steel (S55C) as a mating material.

[0045]

[Effect of the Invention] Since it can decrease that the decomposition carbon produced by electric discharge remains as a lump in an enveloping layer according to this invention as explained in full detail above, a more nearly high-definition enveloping layer can be formed in a metal material list side. It is suitable for raising abrasion resistance, such as metal mold and a gas turbine, thermal resistance, etc.

[Brief Description of the Drawings]

[Drawing 1] It is the figure measuring and showing the film thickness and adhesion power of the electric discharge covering method and other covering methods.

[Drawing 2] It is a figure explaining an example of the equipment used for operation of this invention.

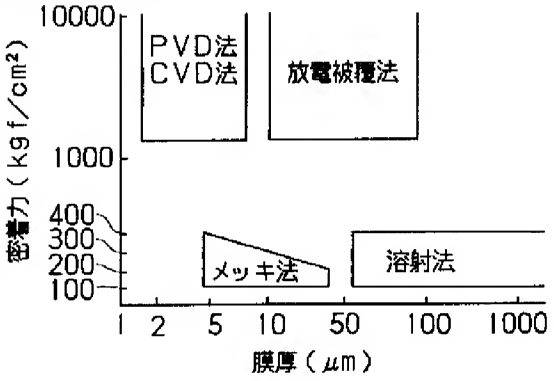
[Drawing 3] It is the photograph for which the cross section (particle structure) of the field analysis result by EPMA of the enveloping layer obtained in the example 1 of an examination is shown, (1) is a secondary electron image, and, as for (2), C and (4) are the field analysis results of Fe W and (3).

[Drawing 4] It is the X diffraction figure of the aluminum die-casting material surface obtained in the example 2 of an examination.

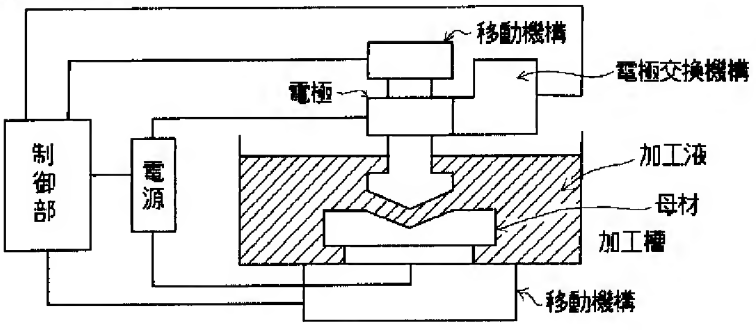
[Drawing 5] It is the figure showing the relation between change of pulse width, the average thickness of an enveloping layer, and the volume ratio of TiC in the example 2 of an examination.

[Drawing 6] It is the figure showing the relation between change of floor to floor time, the average thickness of an enveloping layer, and the volume ratio of TiC in the example 2 of an examination.

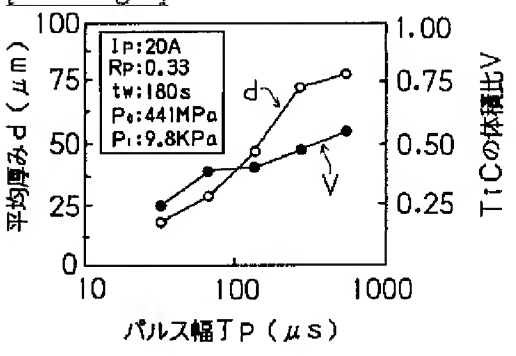
[Drawing 1]



[Drawing 2]



[Drawing 5]



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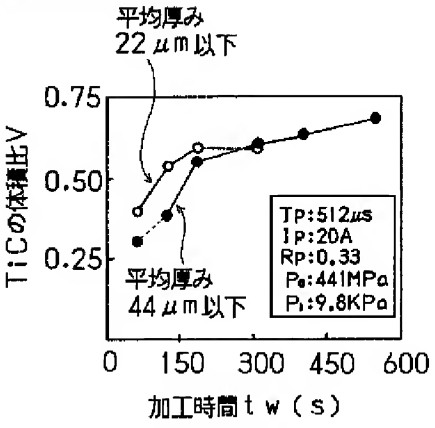
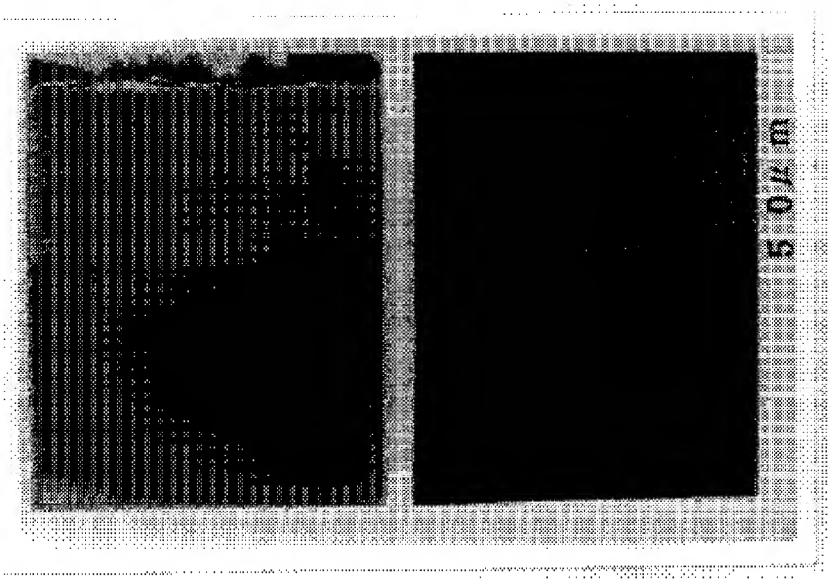


[Drawing 3]

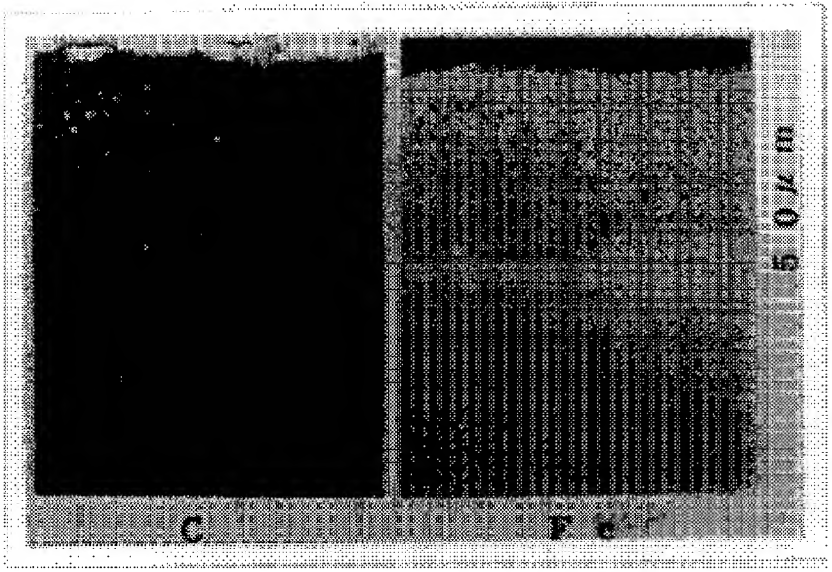
写　　真

(1)　　(2)

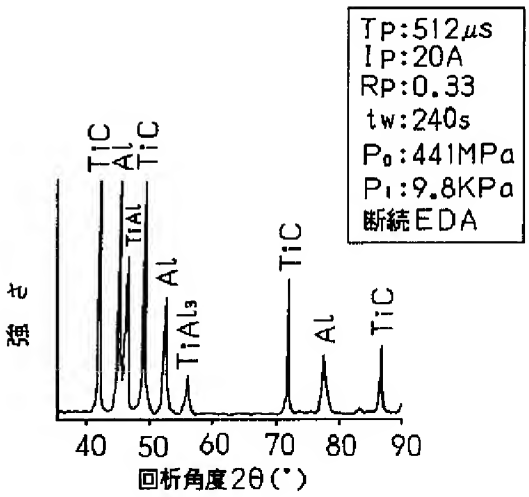


写　　真

(3)　　(4)



[Drawing 4]



[Translation done.]